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Short communication

Transesterification of epoxidized soybean oil to prepare epoxy methyl esters☆

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ABSTRACT

Epoxidized methyl esters were prepared by the transesterification of epoxidized soybean oil (ESBO). The transesterification was complete in 10 min at 50 °C without loss of the epoxide function. Epoxidized methyl esters represent a renewable substrate that is readily converted into surfactants, fuel additives, and other industrial products. The implementation of this reaction will increase the availability of epoxidized methyl esters and promote the development of new biobased products.

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1. Introduction

The demand for biobased products continues to increase as the benefits of using renewable materials are recognized. Oleochemical feedstocks can replace petrochemicals in many applications. This trend reduces the dependence on imported petroleum and promotes the sustainable agricultural initiative. Vegetable oils are one of the most versatile renewable substrates and can be converted into fuels, polymers, and specialty products (Schwab et al., 1987; Gervasio, 1996; Khot et al., 2001). The seed oils obtained from flax and soybeans are particularly useful substrates for the development of biobased products because of the number of unsaturated bonds contained in the component fatty acids which allows a wide range of derivatives to be prepared. Chemical modification of the seed oils at the unsaturated bond sites results in changes to the physical properties of the substrate and allows products to be tailored to meet specific applications.

Epoxidation of the unsaturated bonds that occur along the fatty acid chains of the seed oils produces the more reactive oxirane group. This three-member ring provides a more energetically favorable site for reaction and represents a chemical intermediate for the preparation of derivatives that would be difficult to obtain directly from the unsaturated bond (Dahlke et al., 1995). The epoxidation of vegetable oils is performed on an industrial scale with these materials used primarily for polymers, coatings, adhesives, and similar industrial products (Swern et al., 1945; Khot et al., 2001; Harry-O'kuru et al., 2002). These reports describe products prepared from epoxidized vegetable oils, however, there is recent interest in using

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the vegetable oil esters for new products (Doll and Erhan, 2005; Moser and Erhan, 2006; Kurth et al., 2007). However, the supply of epoxidized methyl esters which could serve as the chemical intermediate for new biobased products is currently limited compared to the commercially available epoxidized vegetable oils.

This study was undertaken to investigate the preparation of epoxidized methyl esters by transesterification of epoxidized vegetable oils. Relatively mild reaction conditions are used for the transesterification of vegetable oil to produce biodiesel, for example (Freedman et al., 1984, 1986; Noureddini and Zhu, 1998). If similar reaction conditions could be applied to transesterify epoxidized vegetable oils without reaction of the epoxy group then a large supply of epoxidized methyl esters would become available and stimulate the development of new biobased products.

2. Materials and methods

2.1. Materials

Epoxidized soybean oil was purchased from Arkema Inc. (Blooming Prairie, MN). Hydrogen bromide/acetic acid, sodium methoxide, chlorobenzene, and methanol were purchased from Sigma–Aldrich Chemicals (St. Louis, MO). Acetic acid was purchased from EM Science Inc. (Gibbstown, NJ). Fatty acid ester, monoglyceride, diglyceride, and triglyceride standards were purchased from Nu-Chek Prep Inc. (Elysian, MN). Refined soybean oil was obtained from Bunge North America Inc. (Decatur, IN). All materials were used as received.

2.2. Transesterification

Reactions were performed in 250 mL flat bottom glass vessels. Epoxidized soybean oil (50 g) was introduced to the glass vessel along with a magnetic stir bar. Sodium methoxide catalyst, 0.5 g (1 wt%), was dissolved in 15 mL methanol and then added to the epoxidized soybean oil in the reactor. This mixture was heated to 50 °C on a hotplate and magnetically stirred at 500 rpm. Samples of the reaction mixture were taken at 10 min intervals for GC and oxirane analyses. The reaction was stopped after 2 h and the reaction mixture was transferred to a separatory funnel to recover the products. The reaction was repeated with refined soybean oil.

2.3. Oxirane oxygen titrations

Titrations were performed to determine the presence of epoxy groups by dissolving 0.3–0.5 g samples of the reaction mixture in 10 mL chlorobenzene/acetic acid (2:1). The mixture was titrated to the endpoint with 33% HBr in acetic acid following AOCS standard test method Cd 9-57 (AOCS, 1998).

2.4. Analysis by gas chromatography

Samples were analyzed with an Agilent 6890 gas chromatograph using a DB-5HT column measuring 15 m × 0.32 mm × 0.1 μm film thickness (J&W Scientific, Folsom, CA). The carrier gas was Helium flowing at 5 mL/min. The oven was programmed from an initial temperature of 50–180 °C at 15 °C/min, increased to 230 at 7°/min, and then to 380 °C at 30 °C/min with a 10 min hold for a total run time of 31 min. Injection volumes were 1 μL with the inlet set to splitless mode. Detection of eluents was made by FID and identified by retention times compared to known standards. Fatty acid esters, monoglycerides, diglycerides, and triglyceride standards were used. Data were collected and processed via Chemstation software (Agilent Technologies Inc., Palo Alto, CA).

3. Results and discussion

The progress of the transesterification reaction was followed by analyzing samples of the reaction mixture at 10 min intervals by GC to monitor the formation of products and by oxirane titration for the presence of epoxy groups. The GC method could detect methyl esters, triglycerides, and the partial transesterification products, monoglycerides and diglycerides in one analysis. Fig. 1 displays the chromatograms obtained for these standards (A) along with samples of transesterified soybean oil (B) and epoxidized soybean oil (C) taken after 10 min of reaction time. Transesterification of the epoxidized vegetable oil proceeded rapidly with complete conversion to the corresponding epoxy methyl esters within the first 10 min as shown by the absence of triglycerides or partial transesterification products. For comparison, the complete transesterification of refined soybean oil required 90 min at these reaction conditions. The difference in reaction times observed between epoxidized and refined soybean oils is attributed to solubility effects. The kinetics of vegetable oil transesterification have been investigated and modeled as a series of reactions that sequentially converts triglycerides to diglycerides, diglyc-

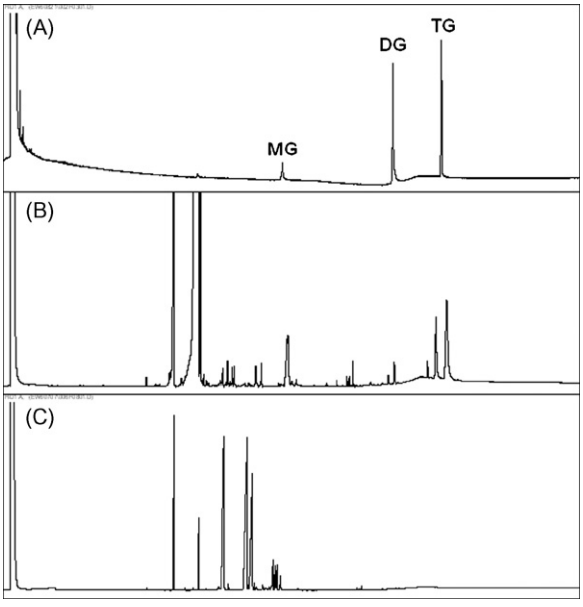

Fig. 1 – Chromatograms of: (A) monoglyceride (MG), diglyceride (DG), and triglyceride (TG) standard compounds; (B) transesterification of refined soybean oil after 10 min; and (C) transesterification of epoxidized soybean oil after 10 min.

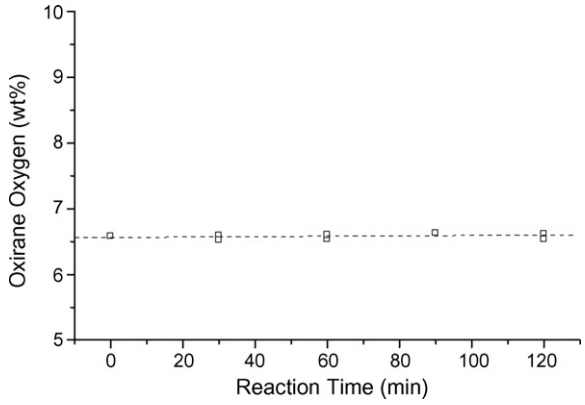

Fig. 2 – Oxirane oxygen values unchanged during transesterification of epoxidized soybean oil.

erides to monoglycerides, and monoglycerides to the esters (Freedman et al., 1986). Soybean oil exhibits a limited solubility in methanol which reduces the rate of the transesterification reaction due to the mass transfer resistance (Boocock et al., 1998). This limited solubility leads to an overall reaction rate that is slower than predicted for a system of sequential reactions in the absence of such mass transfer resistance. In contrast, epoxidized soybean oil rapidly dissolved into methanol. In this case the mass transfer resistance attributed to limited solubility does not exist and a more rapid reaction rate would be observed.

The presence of the epoxy groups were determined by titration for oxirane oxygen. Samples of the reaction mixture were titrated and the corresponding values are plotted in Fig. 2. The horizontal line shows that the number of epoxy groups did not obviously change during the transesterification reaction. However, this was verified by applying analysis of variance (ANOVA) to the oxirane values to statistically test the data for variation. An alpha level of 0.05 was chosen which is a conservative level of significance and is generally accepted to minimize the probability of concluding that there is variation when none exists. The ANOVA calculation returned a p-value of 0.418, which supports the conclusion that no significant variation or differences are present in the oxirane data. If the calculated p-value was less than or equal to the alpha level then one would conclude that there were statistically significant differences in the oxirane values as a result of the transesterification. The reproducibility between replicate titrations for oxirane oxygen values was quite good with less than 0.5% relative standard deviation.

4. Conclusions

These results demonstrate that mild reaction conditions can rapidly convert epoxidized triglycerides to the corresponding methyl esters while preserving the epoxide function. This is an unexpected result given the reactive nature of the oxirane ring. It is evident that base catalysis and relatively low reaction temperatures, 50 °C, are favorable for the transesterification of epoxidized soybean oil. This presents a route to obtain epoxidized methyl esters from epoxidized soybean oil using conventional transesterification technology.

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